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Amending highly acidic blowdown sludge by direct addition of beneficiated alumina refinery residue

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Abstract

This paper examines the relationship between sulfuric acid plant blowdown sludge and alumina refinery residue. Specifically, the research focuses on the neutralization of high levels of acidity in blowdown sludge (i.e., pH <1.0) and the reduction of leachable mercury (average 17.0 mg/L), a major contaminant in this type of industrial sludge at >19,000 mg/kg or 1.9%, using a modified form of alumina refinery residue, also called bauxite residue. Ten experiments on three different types of blowdown sludge were carried out to determine the potential role beneficiated alumina refinery residue might play in neutralizing acid and sequestering leachable mercury into non-bioavailable forms. Results from the study indicate that while all ten treatments either partially or completely neutralized acid and reduced leachable mercury by an average of 68%, only one was successful in reducing mercury to <0.1 mg/L. These findings suggest that alumina refinery residue may be useful in sequestering heavy metals in other forms of industrial solids, sludges and filter cakes.

Keywords: Acidity, mercury, blowdown sludge, sulfuric acid plant, alumina refinery residue

1. Introduction

The adverse human and environmental health effects of mercury (Hg) have been well documented [1] and its potential concentration in global industrial greenhouse gas emissions has been investigated [2]. The highest concentrations of Hg entering the environment occur via emissions from the burning of fossil fuels, particularly in coal-fired power plants which account for about 66% (or 2,200 tonnes per year) of all anthropogenic sources of Hg [3]. However, Hg can also enter the environment via the refining of lead (Pb).

The first of four stages in refining of lead from ore concentrate is sintering, a process designed to inhibit the fine particles in lead concentrate from clogging the blast furnace during smelting. However, in addition to beneficiating ore concentrate in preparation for smelting, sintering also generates sulfur dioxide (SO₂), a noxious greenhouse gas. There are two methods of removing this gas from the lead refining circuit: first, and most commonly, SO₂ can be "directly vented" (i.e., discharged as an untreated, semi-treated or treated gas to the atmosphere via a stack); or secondly, it can be piped to an adjacent acid plant for the manufacture of sulfuric acid (H₂SO₄) [1]. Under most jurisdictions where lead smelters operate, the transfer of SO₂ to an acid plant for the manufacture of sulfuric acid is the preferred and encouraged option due to the potentially damaging environmental effects of SO₂.

There are several main process steps carried out in a sulfuric acid plant, as shown in Figure 1. The SO₂ gas from lead sintering contains fine particulate dust, and as a consequence the gas must be cleaned using a combination of hot gas precipitators followed by a sequence of wet scrubbers. According to the National Pollution Inventory [4], the cleaning of SO₂ can also include electrostatic mist precipitators, with the sequence of each of these cleaning stages varying from plant-to-plant. After cleaning, the solid particulate matter from the dust is concentrated into a waste industrial sludge and then purged from the system using precipitation reagents; this waste, which represents about 0.2-0.5% by weight of the total gas stream (or 2.0-5.0 kg/t of sulfur consumed by the plant), is referred to as acid plant "blowdown sludge".

(The fate of this sludge is central to the present study and will be the subject of further discussion, however little recent worldwide data exist to describe or quantify it, although reports suggest that with 140 sulfuric acid plants, India produces about 5.5 million tonnes of sulfuric acid per year according to its Central Pollution Control Board [5], thus generating an

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estimated 19,000 tonnes of blowdown sludge per year; Berry *et al.* have also reported that the volume of “process residues” from all “smelter off-gas cleaning” in the U.S. was 5.5 million tonnes per year in 2001 [6], surprisingly the most recent year for which statistics on blowdown sludge are available.)

Cleaning SO_2 can produce further dust emissions, which may contain a variety of contaminants, and metal-concentrated fumes, which are discharged to the environment after further scrubbing. Once cleaned, the SO_2 gas is dried to remove any residual water by passing the gas through a drying tower (or series of towers, from which wastewater is discharged to settling ponds) and then passed through converters in which

sulfur dioxide is transformed into sulfur trioxide (SO_3), also a potential atmospheric pollutant and the primary trigger of “acid rain” [7]. The converter stage also generates a range of waste streams, including SO_2 which is sent to a stack for direct venting, and solid-state catalyst residues. Using absorbers, which themselves may discharge further SO_2 to the atmosphere, SO_3 is then dissolved to form 98% strength H_2SO_4 , which is subsequently cooled and stored for later use by the lead smelter or for on-selling to other manufacturing industries, including fertilizer manufacture [8].

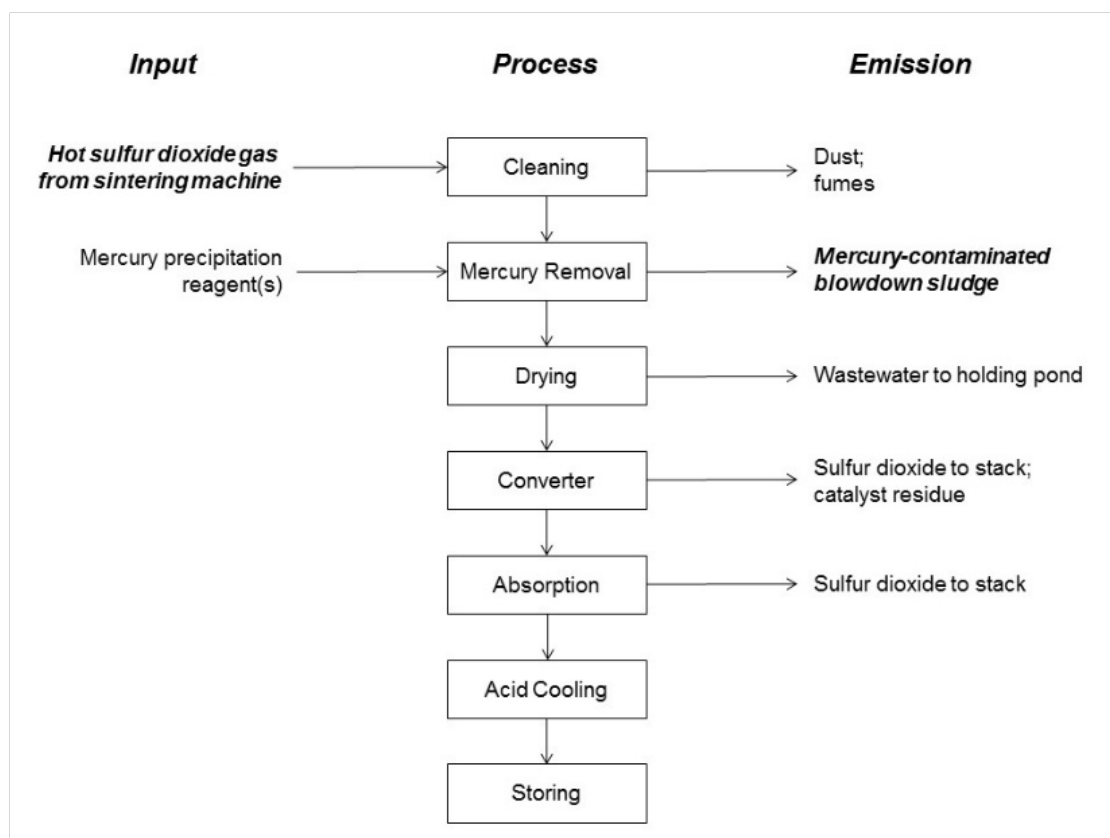


Fig 1: Sulfuric acid plant process flow diagram, showing source of mercury as SO_2 from lead smelter sintering machine and generation of mercury-contaminated blowdown sludge from gas cleaning (source: National Pollution Inventory [4]).

Of most relevance to this study is the finding that a great many ore concentrates used in the refining of lead also contain significantly high concentrations of Hg, as well as other minor metals and metalloids, such as arsenic (As), lead (Pb) and selenium (Se). Some of these Hg concentrations make their way through the lead refining process and are separated from lead bullion during the smelting phase as speiss and matte, while others pass through as dust to the refinery's SO_2 gas.

As noted above, this gas can either be vented directly to the atmosphere or piped to the acid plant, and, if passed through the acid plant, Hg is thereby concentrated into the subsequently formed blowdown sludge. As a consequence, the blowdown sludge of a sulfuric acid plant is extremely high in mercury, and sulfur (S) too is obviously concentrated in the sludge resulting in a highly acidic, hazardous industrial solid waste which requires specialized handling, storage, treatment and disposal. Where viable, the recovery of Hg and S from blowdown sludge is also desirable [6]; where not viable, the treatment of blowdown sludge is required before disposal. The

amendment process of sulfuric acid plant blowdown sludge is the subject of this research paper.

Alumina refinery residue (ARR), sometimes called bauxite residue or “red mud”, is a solid waste by-product from alumina refining. As shown in Figure 2, when extracting alumina (Al_2O_3) from bauxite, a slurry containing approximately 30% solids is generated; this waste slurry, called alumina refinery residue, is discharged from the world's alumina refineries at a rate of about 140 million tonnes per year and is stored in large holding ponds in Australia, China, India, Russia, Brazil, and elsewhere throughout the world [9]. Since the 1960s, ARR has been the subject of an extensive global research program due to its unique chemical and physical properties. For example, ARR can remove hydrogen sulphide and other obnoxious odours and fugitive emissions from municipal and industrial waste sites [10], strengthen self-compacting concrete [11], neutralise acid and bind heavy metals in acid mine drainage [12], and form a coagulant [13]. The integration of ARR into a sustainable industrial future of beneficial waste reuse and the impact of

ARR on other industries have been considered [14, 15], and a detailed life-cycle assessment on the neutralant properties of ARR and its relation to quicklime (i.e., calcium oxide, CaO) has been conducted [16]; importantly, research has shown that ARR is non-toxic [17].

ARR has a pH of ± 12.5 and is a highly alkaline and sodic waste solid; in most international jurisdictions, it is a classified hazardous material due to its acute causticity, which can severely burn skin. When being reused as an environmental ameliorant, ARR must therefore be beneficiated to transform it from a caustic and hazardous material to a benign raw material with fundamentally different chemical and physical properties [18]; other chemical and/or biological agents can be added to

the beneficiated ARR to enhance its original characteristics. These reagents are collectively referred to as derived from “modified alumina refinery residue” or MARR, an example of which is ElectroBind reagent manufactured by Virotec in Australia, described below. (The MARR referred to in this paper is a byproduct of the alumina refining process specifically using the Bayer Process [19]. The process to modify ARR in this study involved adding calcium- and magnesium-based salts to ARR, after which it was rinsed with fresh water in order to reduce its total sodium (Na) concentration and thereby reduce its total alkalinity from $\pm 3,000$ mg/kg to <300 mg/kg and thus its hazardous causticity.)

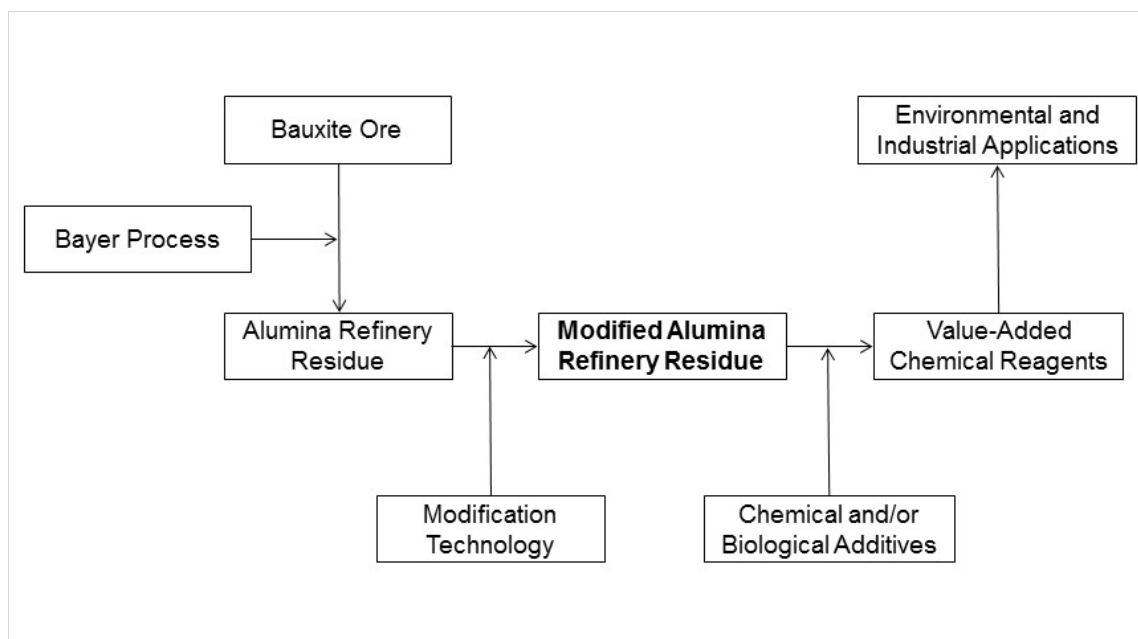


Fig 2: Process flow diagram showing production of modified alumina refinery residue from bauxite and downstream chemical reagents and applications.

MARR is a complex of various chemical compounds, including hematite (Fe_2O_3), boehmite ($\gamma\text{-AlOOH}$), gibbsite ($\text{Al}[\text{OH}]_3$), sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$), and anatase (TiO_2) [15]. Minor compounds include aragonite (CaCO_3), brucite ($\text{Mg}[\text{OH}]_2$), diasporite ($\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), ferrihydrite ($\text{Fe}_5\text{O}_7[\text{OH}] \cdot 4\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hydrocalumite ($\text{Ca}_2\text{Al}[\text{OH}]_7 \cdot 3\text{H}_2\text{O}$), hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3[\text{OH}]_{16} \cdot 4\text{H}_2\text{O}$), and para-aluminohydrocalcite ($\text{CaAl}_2[\text{CO}_3]_2[\text{OH}]_4 \cdot 3\text{H}_2\text{O}$) in descending order of volume by weight. While only present in micro-concentrations, these differently charged molecules in MARR effect long-term isomorphous substitution reactions with metals and metalloids, increasingly occluding them from the environment over time [20]. This characteristic differs from the simple adsorption reactions observed with most industrial chemicals, such as calcium hydroxide ($\text{Ca}[\text{OH}]_2$) and sodium hydroxide (NaOH), that occur because of changes in solution or solids pH leading to reversibility of binding reactions with the passage of time. The isomorphous substitution reactions of MARR result from the positively charged iron-, aluminium-, magnesium- and titanium-based molecules and negatively charged hydroxides and oxyhydroxides which collectively not only initially adsorb metals but subsequently lead to the long-term “sequestering” phenomenon observed with most inorganic species [21].

The role of both ARR and MARR in sequestering metals in wastewater, drinking water and soils has been the subject of considerable worldwide research. For example, Ma *et al.* found the addition of ARR to contaminated water removed cadmium (Cd), copper (Cu) and zinc (Zn) from the liquid stream [22], and Hassan and Davies-McConchie found MARR-impregnated wool removed arsenic (As), Cu and chromium (Cr) from drinking water [23]. In the context of longer term sequestration of metals using the Toxicity Characteristic Leaching Procedure (TCLP) of the U.S. Environmental Protection Agency [24], this author reported that a MARR-derived reagent reduced leachable As, Cr, Cu, and Pb in contaminated mine solids over a 12-month period [25], and a separate long-term study of solids indicated that a MARR-derived reagent reduced the leachability of aluminium (Al) and Pb within two years and Cd and Cu within five years to below the detection limit, and maintained these concentrations through to year 14 [26], thereby confirming that MARR has a long-term sequestering effect on metals. However, no evidence could be found in the scientific literature of any chemical reagents, including both ARR and MARR, ever being used to treat sulphuric acid plant blowdown sludge, or ARR or MARR being specifically used to treat other industrial sludges.

In order to explore the role that alumina refinery residue might play in neutralizing acidic industrial solids and in sequestering metals in blowdown sludge, the present study asked the following research question: Can the direct addition of a chemical reagent derived from MARR to an acid plant blowdown sludge neutralize high levels of acidity and sequester Hg into non-bioavailable forms suitable for disposal to landfill as a low level contaminated waste?

Method

Three x 5.0 kg blowdown sludge samples were obtained from a sulfuric acid plant in Australia; these were labelled Sample #1, Sample #2 and Sample #3. Visual inspection indicated that Sample #1 was a thin, wet slurry with a pink coloration and a $\pm 5\%$ supernatant liquor (SNL) at the top of the settled sample; Sample #2 was a much dryer, sticky pinkish material with a $\pm 2\%$ SNL at the bottom of the sample; and Sample #3 was a dry, homogenous material, with a distinctive dark brown coloration and no SNL at the top or bottom of the sample.

All three samples were sent to a certified laboratory for analysis of pH and total concentrations of the following metals: silver (Ag); As; barium (Ba); Cd; cobalt (Co); Cr; Cu; Hg; molybdenum (Mo); nickel (Ni); Pb; antimony (Sb); selenium (Se); and Zn. Samples were tested for total metals using either inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS), as appropriate. Based on total metals concentrations above 500 mg/kg, analyses of leachable Cu and Hg using TCLP were also carried out at this stage. Findings from the analysis of each sample are presented in Table 1.

Table 1: Analytical data on three separate pre-treated sulfuric acid plant blowdown sludge types (Samples #1-3) and one homogenized sludge type (Sample #4).

Parameter	Sample #1	Sample #2	Sample #3	Sample #4
Moisture Content (%)	22	7	0	—
pH	1.1	0.1	0.1	0.1
EC	—	—	—	488
Ag (mg/kg)	—	—	—	—
As (mg/kg)	12	6.4	0.4	6.3
Ba (mg/kg)	1.1	1.5	4.7	2.4
Cd (mg/kg)	5.4	0.92	1.2	7.5
Co (mg/kg)	0.55	0.13	0.69	0.45
Cr (mg/kg)	49	5.9	26	27
Cu (mg/kg)	43	14	790	282
Leachable Cu (mg/L)	2.2	0.6	37	11.9
Hg (mg/kg)	19,100	14,700	2,120	11,973
Leachable Hg (mg/L)	29	19	4.1	20
Mo (mg/kg)	5.2	0.7	2.5	2.8
Ni (mg/kg)	35	6.4	44	28
Pb (mg/kg)	42	22	160	75
Sb (mg/kg)	2.6	0.87	0.74	1.4
Se (mg/kg)	340	335	18	231
Zn (mg/kg)	200	79	63	114

† Below the limit of detection

From Table 1 it can be seen that Sample #1 had a moisture content of 22% and a pH of 1.1, Sample #2 had a moisture content of 7% and pH of 0.1, and Sample #3 contained no moisture and a pH of 0.1. Metal concentrations of most significance were Cu in Sample #3 at 790 mg/kg and Hg at 19,100 mg/kg in Sample #1, 14,700 mg/kg in Sample #2, and 2,120 mg/kg in Sample #3. In order to determine optimal chemical addition rates, titration curves were carried out for each sample, and the results from these titrations can be seen in Figures 3, 4 and 5.

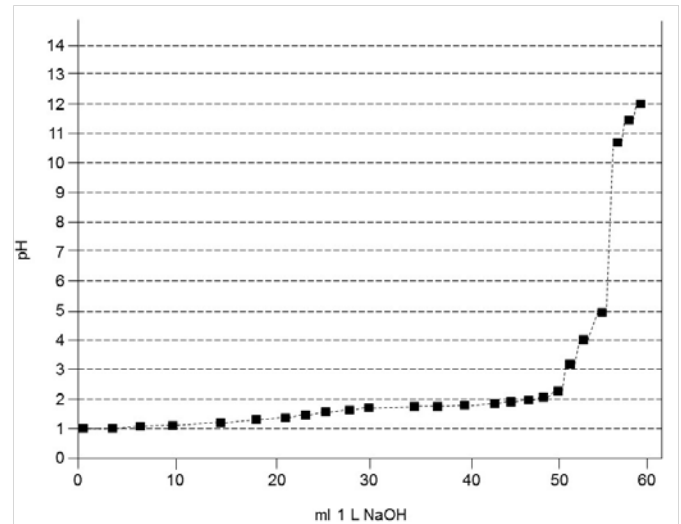


Fig 3: Titration curve for Sample #1.

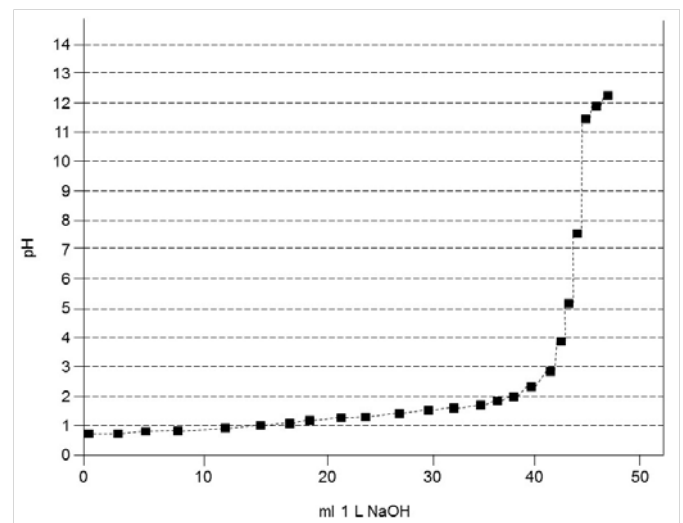


Fig 4: Titration curve for Sample #2.

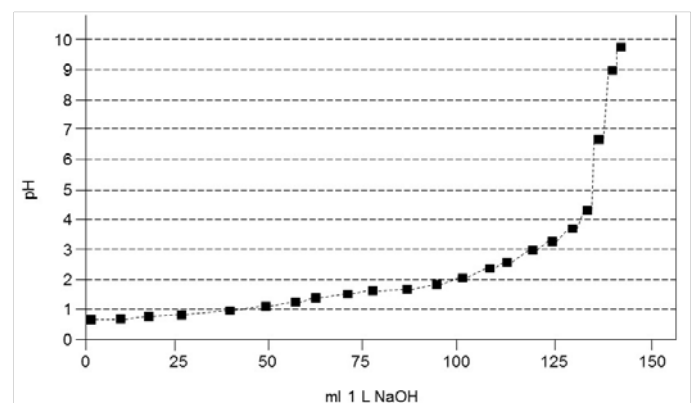


Fig 5: Titration curve for Sample #3.

As shown in Table 1, a fourth sample was created by mixing 1.0 kg of Samples #1, #2 and #3 separately until each was visually homogeneous and then all three samples were composited for 30 minutes into one homogenous 3.0 kg sample and labeled Sample #4. Analysis of the homogenized Sample #4 indicated a pH of 0.1, electrical conductivity (EC) of 488 mS/cm, and a leachable Hg concentration of 20 mg/L. In order for blowdown sludge to be considered acceptable for disposal to landfill as a low-level contaminated waste in Australia, a treatment target of < 0.1 mg/L leachable Hg was determined.

Based on the titration curves presented in Figures 3, 4 and 5, two different blends of ElectroBind reagent were developed and applied, one consisting of 20% MARR and 80% magnesium oxide (MgO) used primarily for pH adjustment (ElectroBind A) and a second consisting of 80% MARR and 20% MgO used primarily for metal sequestration (ElectroBind B). Both ElectroBind A and B were directly added as dry powders. The presence of hydroxides and oxy-hydroxides in MARR contribute to its acid neutralizing capacity (ANC). For example, sixteen hydroxides in hydrotalcite, seven oxy-hydroxides in ferrihydrite, and four hydroxides in p-alumunohydrocalcite contribute to the ANC of MARR, the subject of prior research [27]. Studies have indicated the ANC of MARR is about 3.6 mmoles of acid/kg at pH 8.0, but can be as high as 17.0 mmoles of acid/kg at pH 5.5 (for example, hydrotalcite alone has an ANC of 28.26 mmoles of acid/kg, according to Lin *et al.* [28]); with the addition of other acid-neutralizing chemicals, such as MgO, these levels of ANC can be adjusted upward as required. The following test protocols were developed for Samples #1, #2, #3 and #4.

After dividing Sample #1 into three x 300 g samples labeled Samples #1A, #1B, and #1C, **Treatment A:** Mix Sample #1A until visually homogeneous; add 78 g of ElectroBind A slowly to 300 g of sample (i.e., 260g/kg; note, heat is generated by this process as acute acidity is neutralized); mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 76 g of ElectroBind B (ratio of 5:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals [tin (Sn), thorium (Th) and vanadium (V) were included in post-treatment analysis]. **Treatment B:** Mix Sample #1B until visually homogeneous; add 78 g of ElectroBind A slowly to 300 g of sample; mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 189 g of ElectroBind B (ratio of 2:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals. **Treatment C:** Mix Sample #1C until visually homogeneous; add 78 g of ElectroBind A slowly to 300 g of sample; mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 378 g of ElectroBind B (ratio of 1:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals.

After dividing Sample #2 into three x 300g samples labeled Samples #2A, #2B, and #2C, **Treatment D:** Mix Sample #2A until visually homogeneous; add 60 g of ElectroBind A slowly to 300 g of sample (i.e., 200g/kg; note, heat is generated by this process as acute acidity is neutralized); mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 72 g of ElectroBind B (ratio of 5:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals. **Treatment E:** Mix Sample #2B until visually homogeneous; add 60 g of ElectroBind A slowly to 300 g of sample; mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture

add 180 g of ElectroBind B (ratio of 2:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals.

Treatment F: Mix Sample #2C until homogeneous; add 60 g of ElectroBind A slowly to 300 g of sample; mix thoroughly by hand until visually homogenous; let stand for 24 hours; to this mixture add 360 g of ElectroBind B (ratio of 1:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals.

After dividing Sample #3 into three x 300g samples labeled Samples #3A, #3B, and #3C, **Treatment G:** Mix Sample #3A until visually homogeneous; add 75 g of ElectroBind A slowly to 300 g of sample (i.e., 250g/kg, note heat is generated by this process as acute acidity is neutralized); mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 75 g of ElectroBind B (ratio of 5:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals. **Treatment H:** Mix Sample #3B until visually homogeneous; add 75 g of ElectroBind A slowly to 300 g of sample; mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 188 g of ElectroBind B (ratio of 2:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals.

Treatment I: Mix Sample #3C until visually homogeneous; add 75 g of ElectroBind A slowly to 300 g of sample; mix thoroughly by hand until homogenous; let stand for 24 hours; to this mixture add 375 g of ElectroBind B (ratio of 1:1); let stand for 24 hours; analyze for pH, EC, and total and leachable metals.

Treatment J: As a result of mixing and letting Sample #4 stand for 24 hours, it was noted that three distinctly stratified layers had formed in the sludge, namely a bottom layer of sludge, a top layer of sludge, and SNL on top of the sludge; remove 100 g sub-samples of top and bottom layers sludge, homogenize and analyze for pH, electrical conductivity (EC), total metal concentrations, and leachable Hg (as shown in Table 1); to homogenized Sample #4 add 1 L of fresh water and mix for ten minutes; add 225 g of ElectroBind A slowly to approximately 3.0 kg of Sample #4 and mix thoroughly until a pH of 7.0 is reached; note heat is generated by this process as acute acidity is neutralized; let stand for 24 hours; decant the approximately 1.0 L of SNL on top of the sludge; to the remaining settled sludge add 3.0 kg of ElectroBind B (approximate ratio of 1:1) and mix thoroughly until visually homogeneous; let stand for 24 hours; analyze for pH, EC and leachable Hg in top and bottom layers of sludge and SNL.

Results and Discussion

Table 2 presents the findings for Treatments A-J. For Treatments A, B and C, pH rose from 1.1 to 11.1, 9.2 and 3.6. These findings are curious given that the amount of alkalizing agent used in Treatment C was greater than Treatment B, and Treatment B was greater than Treatment A, yet pH declined as more reagents were added.

The total Cu concentration in Sample #1 before treatment was 43 mg/kg and after treatment remained stable at 45 mg/kg, 53 mg/kg and 47 mg/kg respectively, meaning that the addition of ElectroBind did not change the total Cu concentrations in treated blowdown sludge; significant dilution of total Cu as a result of the 5:1, 2:1, and 1:1 addition rates of ElectroBind was not observed, possibly due to the fact that seven global samples of ARR had previously been found to contain an average of 46 mg/kg of Cu [21]. However, leachable Cu was reduced from 2.2 mg/L before treatment to 0.01 mg/L, 0.04 mg/L and 0.63

mg/L by each treatment, representing reductions of 99%, 98% and 71%. This finding, too, is curious given that the higher reagent addition rates appear to have produced declining rates of Cu sequestration.

Furthermore, the total Hg concentration in Sample #1 before treatment was 19,100 mg/kg and after treatment was reduced to 5,420 mg/kg, 7,200 mg/kg and 9,980 mg/kg, meaning that the addition of ElectroBind reduced total Hg concentrations in the treated blowdown sludge by 72%, 62% and 48% which

demonstrates the Hg sequestering properties of ElectroBind, although again it is curious that with greater addition of ElectroBind the Hg sequestering effect was reversed. However, leachable Hg was consistently reduced from 29 mg/L before treatment to 5.6 mg/L, 5.8 mg/L and 6.0 mg/L by each treatment, representing reductions of 81%, 81% and 80%. However, Treatments A-C did not answer the research question in the affirmative.

Table 2: Post-treatment analytical data for Treatments A-J.

	Treatments A, B and C			Treatments D, E and F			Treatments G, H and I			Treatment J		
Parameter	Sample #1A	Sample #1B	Sample #1C	Sample #2A	Sample #2B	Sample #2C	Sample #3A	Sample #3B	Sample #3C	Sample #4		
										Top Layer	Bottom Layer	SNL
pH	11.1	9.2	3.6	8.5	5.5	1.7	6.0	4.1	9.8	8.7	8.7	8.7
EC (mS/cm)	50	48	48	206	13	29	12	13	21	14.9	14.8	172
Total Ag (mg/kg)	0.23	0.23	0.35	0.14	0.19	0.17	2.5	2.8	0.59	—	—	—
Leachable Ag (mg/L)	<0.002 [†]	<0.002 [†]	<0.002 [†]	<0.002 [†]	<0.002 [†]	<0.002 [†]	<0.002 [†]	0.05	<0.002 [†]	—	—	—
Total As (mg/kg)	1.1	2.6	11	0.93	13	5.6	0.39	2.8	0.24	—	—	—
Leachable As (mg/L)	0.008	0.003	0.001	0.004	0.004	0.009	0.005	0.06	0.005	—	—	—
Total Ba (mg/kg)	4.4	5.1	3.1	4.9	5.1	2.6	6.3	4.9	6.4	—	—	—
Leachable Ba (mg/L)	<0.005 [†]	<0.005 [†]	0.04	<0.005 [†]	<0.005 [†]	0.05	0.005	0.02	<0.005 [†]	—	—	—
Total Cd (mg/kg)	1.7	2.3	2.8	0.4	0.45	0.79	0.19	0.15	0.17	—	—	—
Leachable Cd (mg/L)	0.0007	0.002	0.09	0.005	0.0007	0.03	0.004	0.02	<0.0005 [†]	—	—	—
Total Co (mg/kg)	5.8	4.9	2.5	5.9	8.2	2.1	6.3	6.4	4.6	—	—	—
Leachable Co (mg/L)	0.002	0.004	0.02	0.002	0.007	0.06	0.03	0.06	0.003	—	—	—
Total Cr (mg/kg)	49	58	64	39	147	34	50	80	42	—	—	—
Leachable Cr (mg/L)	0.01	0.01	0.38	0.007	0.007	0.44	0.04	0.62	<0.005 [†]	—	—	—
Total Cu (mg/kg)	45	53	47	36	32	55	298	388	324	—	—	—
Leachable Cu (mg/L)	0.01	0.04	0.63	0.25	0.25	0.45	0.39	5.3	0.04	—	—	—
Total Hg (mg/kg)	5,420	7,200	9,980	5,480	7,560	10,320	292	40	339	—	—	—
Leachable Hg (mg/L)	5.6	5.8	6.0	6.0	6.0	6.5	3.4	6.8	1.8	<0.01 [†]	<0.01 [†]	<0.01 [†]
Total Mo (mg/kg)	0.3	0.68	3.5	0.08	0.72	0.54	0.11	0.38	0.12	—	—	—
Leachable Mo (mg/L)	0.08	0.03	0.01	<0.005 [†]	<0.005 [†]	<0.005 [†]	<0.005 [†]	0.01	0.01	—	—	—

Total Ni (mg/kg)	18	21	23	10	15	7.1	20	27	19	—	—	—
Leachable Ni (mg/L)	0.02	0.27	0.86	0.07	0.07	0.23	0.49	0.8	0.01	—	—	—
Total Pb (mg/kg)	61	74	107	16	17	19	26	13	18	—	—	—
Leachable Pb (mg/L)	<0.002 [†]	<0.002 [†]	0.04	0.002	0.008	0.03	0.004	0.08	<0.002 [†]	—	—	—
Total Sb (mg/kg)	0.06	0.07	0.25	0.03	0.08	0.06	0.03	0.08	0.03	—	—	—
Leachable Sb (mg/L)	0.007	0.006	0.001	0.001	0.001	0.001	<0.001 [†]	0.002	0.001	—	—	—
Total Se (mg/kg)	9.9	25	212	7.2	160	117	0.09	1.3	0.15	—	—	—
Leachable Se (mg/L)	<0.002 [†]	0.01	<0.002 [†]	0.01	0.01	0.01	0.01	0.006	0.02	—	—	—
Total Sn (mg/kg)	0.32	0.32	1.6	0.17	2.2	0.92	0.5	1.3	0.31	—	—	—
Leachable Sn (mg/L)	<0.1 [†]	<0.1 [†]	<0.1 [†]	<0.1 [†]	<0.1 [†]	<0.1 [†]	<0.1 [†]	<0.1 [†]	<0.1 [†]	—	—	—
Total Th (mg/kg)	0.14	0.18	0.23	0.07	0.08	0.11	0.05	0.05	0.04	—	—	—
Leachable Th (mg/L)	<0.001 [†]	<0.001 [†]	<0.001 [†]	<0.001 [†]	<0.001 [†]	0.001	<0.001 [†]	<0.001 [†]	<0.001 [†]	—	—	—
Total V (mg/kg)	56	55	37	58	148	33	52	63	35	—	—	—
Leachable V (mg/L)	0.14	0.04	<0.001 [†]	0.02	0.02	0.16	0.02	0.01	0.02	—	—	—
Total Zn (mg/kg)	78	104	134	40	54	73	28	34	29	—	—	—
Leachable Zn (mg/L)	0.01	0.14	—	0.16	0.16	3.5	0.13	0.95	0.01	—	—	—

[†] Below the limit of detection

For Treatments D, E and F, pH rose from 0.1 to 8.5, 5.5 and 1.7. As was the case for Treatments A-C, these findings are also unusual given that the amount of alkalizing agent used in Treatment F was greater than Treatment E, and Treatment E was greater than Treatment D, yet pH declined even more dramatically as more reagent was added, the reverse of expected trends and contrary to titration analysis. The total Cu concentration in Sample #2 before treatment was 14 mg/kg and increased after treatment to 36 mg/kg, 32 mg/kg and 55 mg/kg respectively, meaning that the addition of ElectroBind increased the total Cu concentrations in treated blowdown sludge; as noted above, this was likely due to the fact that MARR contains Cu. However, leachable Cu was reduced from 0.6 mg/L before treatment to 0.25 mg/L for Treatments D and E, and 0.45 mg/L for Treatment F, representing reductions of 58% and 25% respectively. This finding, too, is curious given that the higher reagent addition rates appear to have produced declining rates of Cu sequestration.

The total Hg concentration in Sample #2 before treatment was 14,700 mg/kg and after treatment was reduced to 5,420 mg/kg, 7,200 mg/kg and 9,980 mg/kg, meaning that the addition of ElectroBind reduced total Hg concentrations in the treated blowdown sludge by 72%, 62% and 48% respectively; again, greater addition rates of ElectroBind resulted in declining

sequestration, the reverse of previously observed reaction trends. However, leachable Hg was consistently reduced from 19 mg/L before treatment to 6.0 mg/L for Treatments D and E and 6.5 mg/L for Treatment F, representing reductions of 69% and 66% respectively. Treatments D-F did not, however, answer the research question in the affirmative.

For Treatments G, H and I, pH rose from 0.1 to 6.0, 4.1 and 9.8. As was the case for Treatments A-C and D-F, while more consistent, these pH findings are counterintuitive given that the amount of alkalizing agent used in Treatment H was greater than Treatment G, yet pH was lower in Treatment H than Treatment G. The total Cu concentration in Sample #3 before treatment was 790 mg/kg and decreased consistently after treatment to 298 mg/kg, 388 mg/kg and 324 mg/kg respectively, meaning that the addition of ElectroBind decreased the total Cu concentrations in treated blowdown sludge by 62%, 51% and 59%, mostly due to diluting effects. However, leachable Cu in these treatments was reduced from 37 mg/L before treatment to 0.39 mg/L for Treatment G, 5.3 mg/L for Treatment H, and 0.04 mg/L for Treatment I, representing reductions of 99%, 86% and 99%. Curiously, higher addition rates of ElectroBind did not increase Cu sequestration, as was the case for Treatments A-F.

The total Hg concentration in Sample #3 before treatment was 2,120 mg/kg and after treatment was reduced to 292 mg/kg, 40 mg/kg and 339 mg/kg, meaning that the addition of ElectroBind reduced total Hg concentrations in the treated blowdown sludge by 86%, 98% and 84% respectively, probably due to dilution. However, Treatments G-I only randomly affected leachable Hg, reducing it from 4.1 mg/L before treatment to 3.4 mg/L after Treatment G (a 17% reduction), increasing it to 6.8 mg/L after Treatment H (a 60% increase), and reducing to 1.8 mg/L after Treatment I (an 88% reduction). Therefore, Treatments G-I did not answer the research question in the affirmative.

It would appear that moisture content before treatment did not affect treatment outcomes, as leachable Hg concentrations were uniformly consistent across all samples, despite Sample #1 containing 22% moisture, Sample #2 containing 7% moisture and Sample #3 containing no moisture. In industrial solids treatment, the presence of moisture at 10-20% is generally viewed as advantageous because it aids in the physical blending of and contact between reagent and contaminant, and thereby improves metal sequestration. However this phenomenon apparently did not factor into the Hg outcomes observed in this experiment; if anything the two higher reduction levels were recorded when the sample:reagent interface was driest in Treatments G and I.

The observation that MARR sequestered Hg more effectively when total Hg concentrations were highest is also counterintuitive and contrary to earlier reports for this material. For example, the sequestration rates of Treatments A-C averaged 81% when total Hg was 19,100 mg/kg, sequestration rates of Treatments D-F averaged 68% when total Hg was 14,700 mg/kg, and sequestration rates Treatments G-I averaged 55% when total Hg was just 2,120 mg/kg. One possible explanation could be that Hg in each blowdown sludge sample had a different valency or was present in the blowdown sludge samples in different compounds or alloys, for example as a mercuric sulfide (HgS) in one but not the other. Further work is required to investigate these sequestration rate anomalies, and to better understand why higher amounts of neutralants would produce lower rates of acid neutralization.

The most significant changes occurred with Treatment J, despite this treatment only differing from Treatments A-I in the way blowdown sludge was pre-soaked and treated in 3:1 water with the liquid phase decanted after 24 hours. In this experiment, pH rose from 0.1 in the homogenized sample before treatment to 8.7 in each of the top and bottom layers of the treated sludge, as well as to 8.7 in the decanted SNL. EC was reduced from 488 mS/cm to an average of 14.9 mS/cm in the top and bottom layers of sludge (a 97% reduction) and 172 mS/cm in the SNL (a 65% reduction). Given that samples of ARR from around the world had previously been shown to have an EC of approximately 10.5 [21], this finding indicates that MARR did not contribute significantly to these conductivity results and that EC was likely reduced in this experiment as a result of Treatment J; at least some of the residual alkalinity of MARR was transferred to the flushing solution as indicated by the higher EC in the SNL than in both the top and bottom layers of sludge.

The leachable Hg concentration of 20 mg/L before treatment in Sample #4 was reduced to <0.01 mg/L, the limit of detection, in the top and bottom layers of the sludge as well as in the SNL

(all 99% reductions) as a result of Treatment J. No evidence was found that the pre-soaking stage of Treatment J, which differed from the other treatments, was responsible for removing Hg from the solid phase to the liquid phase, as post-treatment leachable concentrations of Hg in the top and bottom layers of sludge were the same as the post-treatment concentration of the SNL. The leachable Hg findings of Treatment J differ significantly from those of Treatments A-C (average leachable Hg reduction of 81% reduction), Treatments D-F (average 68% reduction), and Treatments G-I (average 55% reduction). It can, however, be concluded that Treatment J answered the research question in the affirmative.

Conclusion

To this author's knowledge, the present study represents the first systematic investigation into the chemical properties of sulfuric acid plant blowdown sludge and the first to consider their remediation using modified alumina refinery residue.

In this study, some treatments using MARR-derived chemical reagents were successful in neutralizing high levels of acidity in blowdown sludge, although the data on acidity leave many unanswered questions about the chemical reactions promulgated by MARR in highly acidic environments. These MARR reagents sequestered Cu and Hg by an average of 68%, but in some cases *higher* addition rates mysteriously resulted in *lower* levels of sequestration. However, with the homogenization of the three separate blowdown sludge samples and the addition and subsequent decanting of supernatant liquor from the sludge, MARR fully sequestered Hg to below the leachability target of < 0.01 mg/kg.

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